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B1X 6B1 6B7 6B6 6B5 6B4 6FA 6FY 6G1 6I4 6K 6L 6M 6N 6P 6Q 6R 6S 6T 6U 6V 6W 6X 6Y 6Z 6AA 6AB 6AC 6AD 6AE 6AF 6AG 6AH 6AI 6AJ 6AK 6AL 6AM 6AN 6AO 6AP 6AQ 6AR 6AS 6AT 6AU 6AV 6AW 6AX 6AY 6AZ 6BA 6BB 6BC 6BD 6BE 6BF 6BG 6BH 6BI 6BJ 6BK 6BL 6BM 6BN 6BO 6BP 6BQ 6BR 6BS 6BT 6BU 6BV 6BW 6BX 6BY 6BZ 6CA 6CB 6CC 6CD 6CE 6CF 6CG 6CH 6CI 6CJ 6CK 6CL 6CM 6CN 6CO 6CP 6CQ 6CR 6CS 6CT 6CU 6CV 6CW 6CX 6CY 6CZ 6DA 6DB 6DC 6DD 6DE 6DF 6DG 6DH 6DI 6DJ 6DK 6DL 6DM 6DN 6DO 6DP 6DQ 6DR 6DS 6DT 6DU 6DV 6DW 6DX 6DY 6DZ 6EA 6EB 6EC 6ED 6EE 6EF 6EG 6EH 6EI 6EJ 6EK 6EL 6EM 6EN 6EO 6EP 6EQ 6ER 6ES 6ET 6EU 6EV 6EW 6EX 6EY 6EZ 6FA 6FB 6FC 6FD 6FE 6FF 6FG 6FH 6FI 6FJ 6FK 6FL 6FM 6FN 6FO 6FP 6FQ 6FR 6FS 6FT 6FU 6FV 6FW 6FX 6FY 6FZ 6GA 6GB 6GC 6GD 6GE 6GF 6GG 6GH 6GI 6GJ 6GK 6GL 6GM 6GN 6GO 6GP 6GQ 6GR 6GS 6GT 6GU 6GV 6GW 6GX 6GY 6GZ 6HA 6HB 6HC 6HD 6HE 6HF 6HG 6HH 6HI 6HJ 6HK 6HL 6HM 6HN 6HO 6HP 6HQ 6HR 6HS 6HT 6HU 6HV 6HW 6HX 6HY 6HZ 6IA 6IB 6IC 6ID 6IE 6IF 6IG 6IH 6IJ 6IK 6IL 6IM 6IN 6IO 6IP 6IQ 6IR 6IS 6IT 6IU 6IV 6IW 6IX 6IY 6IZ 6JA 6JB 6JC 6JD 6JE 6JF 6JG 6JH 6JI 6JJ 6JK 6JL 6JM 6JN 6JO 6JP 6JQ 6JR 6JS 6JT 6JU 6JV 6JW 6JX 6JY 6JZ 6KA 6KB 6KC 6KD 6KE 6KF 6KG 6KH 6KI 6KJ 6KK 6KL 6KM 6KN 6KO 6KP 6KQ 6KR 6KS 6KT 6KU 6KV 6KW 6KX 6KY 6KZ 6LA 6LB 6LC 6LD 6LE 6LF 6LG 6LH 6LI 6LJ 6LK 6LM 6LN 6LO 6LP 6LQ 6LR 6LS 6LT 6LU 6LV 6LW 6LX 6LY 6LZ 6MA 6MB 6MC 6MD 6ME 6MF 6MG 6MH 6MI 6MJ 6MK 6ML 6MM 6MN 6MO 6MP 6MQ 6MR 6MS 6MT 6MU 6MV 6MW 6MX 6MY 6MZ 6NA 6NB 6NC 6ND 6NE 6NF 6NG 6NH 6NI 6NJ 6NK 6NL 6NM 6NN 6NO 6NP 6NQ 6NR 6NS 6NT 6NU 6NV 6NW 6NX 6NY 6NZ 6OA 6OB 6OC 6OD 6OE 6OF 6OG 6OH 6OI 6OJ 6OK 6OL 6OM 6ON 6OO 6OP 6OQ 6OR 6OS 6OT 6OU 6OV 6OW 6OX 6OY 6OZ 6PA 6PB 6PC 6PD 6PE 6PF 6PG 6PH 6PI 6PJ 6PK 6PL 6PM 6PN 6PO 6PP 6PQ 6PR 6PS 6PT 6PU 6PV 6PW 6PX 6PY 6PZ 6QA 6QB 6QC 6QD 6QE 6QF 6QG 6QH 6QI 6QJ 6QK 6QL 6QM 6QN 6QO 6QP 6QQ 6QR 6QS 6QT 6QU 6QV 6QW 6QX 6QY 6QZ 6RA 6RB 6RC 6RD 6RE 6RF 6RG 6RH 6RI 6RJ 6RK 6RL 6RM 6RN 6RO 6RP 6RQ 6RR 6RS 6RT 6RU 6RV 6RW 6RX 6RY 6RZ 6SA 6SB 6SC 6SD 6SE 6SF 6SG 6SH 6SI 6SJ 6SK 6SL 6SM 6SN 6SO 6SP 6SQ 6SR 6SS 6ST 6SU 6SV 6SW 6SX 6SY 6SZ 6TA 6TB 6TC 6TD 6TE 6TF 6TG 6TH 6TI 6TJ 6TK 6TL 6TM 6TN 6TO 6TP 6TQ 6TR 6TS 6TT 6TU 6TV 6TW 6TX 6TY 6TZ 6UA 6UB 6UC 6UD 6UE 6UF 6UG 6UH 6UI 6UJ 6UK 6UL 6UM 6UN 6UO 6UP 6UQ 6UR 6US 6UT 6UU 6UV 6UW 6UX 6UY 6UZ 6VA 6VB 6VC 6VD 6VE 6VF 6VG 6VH 6VI 6VJ 6VK 6VL 6VM 6VN 6VO 6VP 6VQ 6VR 6VS 6VT 6VU 6VV 6VW 6VX 6VY 6VZ 6WA 6WB 6WC 6WD 6WE 6WF 6WG 6WH 6WI 6WJ 6WK 6WL 6WM 6WN 6WO 6WP 6WQ 6WR 6WS 6WT 6WU 6WV 6WW 6WX 6WY 6WZ 6XA 6XB 6XC 6XD 6XE 6XF 6XG 6XH 6XI 6XJ 6XK 6XL 6XM 6XN 6XO 6XP 6XQ 6XR 6XS 6XT 6XU 6XV 6XW 6XX 6XY 6XZ 6YA 6YB 6YC 6YD 6YE 6YF 6YG 6YH 6YI 6YJ 6YK 6YL 6YM 6YN 6YO 6YP 6YQ 6YR 6YS 6YT 6YU 6YV 6YW 6YX 6YY 6YZ 6ZA 6ZB 6ZC 6ZD 6ZE 6ZF 6ZG 6ZH 6ZI 6ZJ 6ZK 6ZL 6ZM 6ZN 6ZO 6ZP 6ZQ 6ZR 6ZS 6ZT 6ZU 6ZV 6ZW 6ZX 6ZY 6ZZ

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(54) Process for the production of filter elements based on polysulphonate

(52) In the production of polysulphonate-based filter elements cell structure reproducibility is improved by carrying out coagulation and stabilization of the polysulphonate solution in a liquid bath over a period of about 30 seconds to 240 seconds.

a) at temperatures from below 0°C to about 15°C for producing filter elements of pore size 0.1 nm to 1 nm suitable for the separation of macromolecules (ultrafiltration), or

b) at temperatures from about 15°C to about 45°C for producing filter elements of asymmetric cell structure and pore size 0.05 µm to 10 µm suitable for the separation of particles (microfiltration) or

c) at temperatures from about 45°C to 80°C for the production of filter elements of a symmetric cell structure and a pore size 0.05 µm to 10 µm for the separation of particles (microfiltration).

the filter element being subsequently washed in a liquid bath.

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0.6 Rate of through flow of water Fig.1

$\left[\frac{\text{ml}}{\text{cm}^2 \text{min}} \right]$

Mixture 1

Mixture 2

$T [^{\circ}\text{C}]$

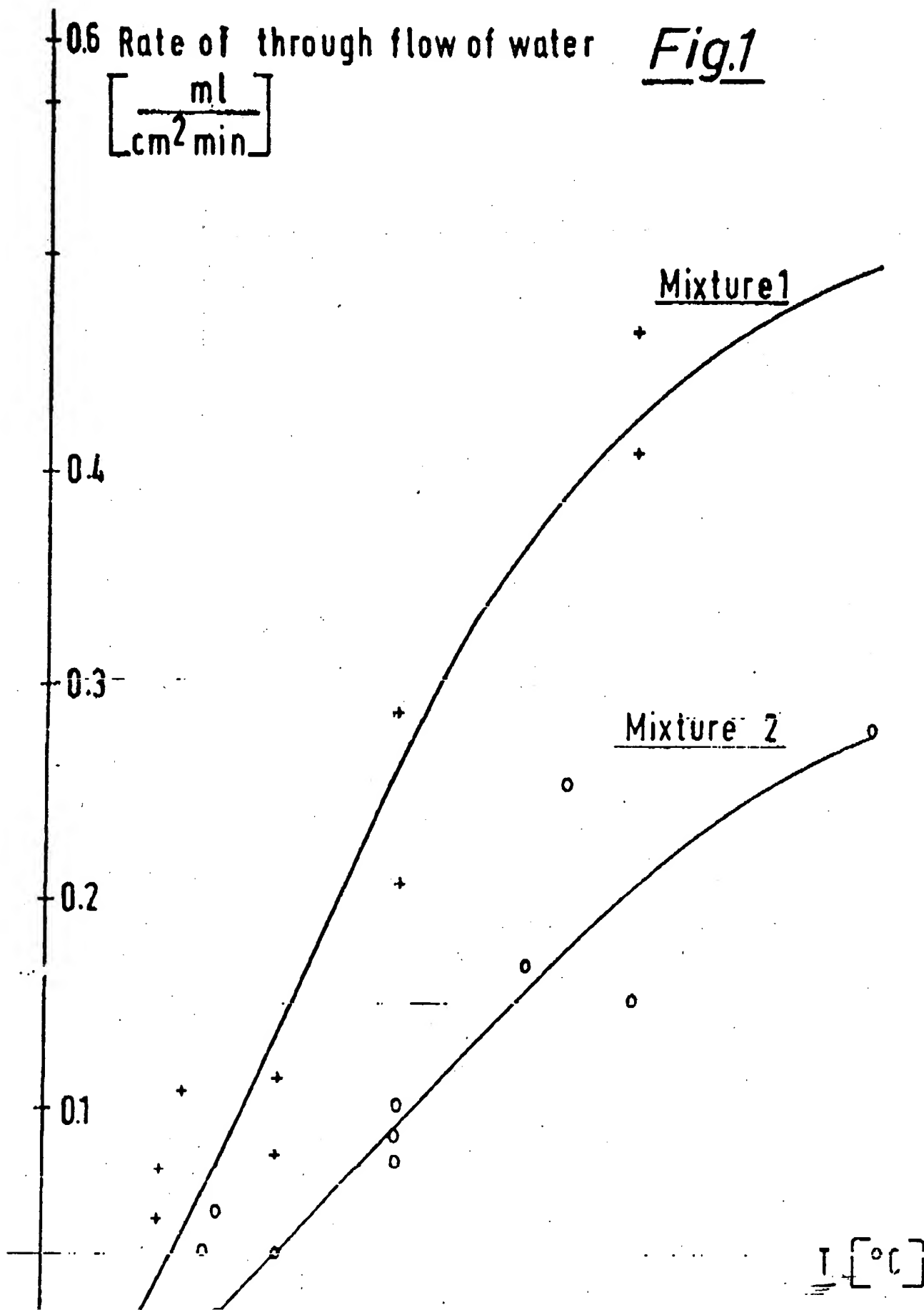


Fig.2

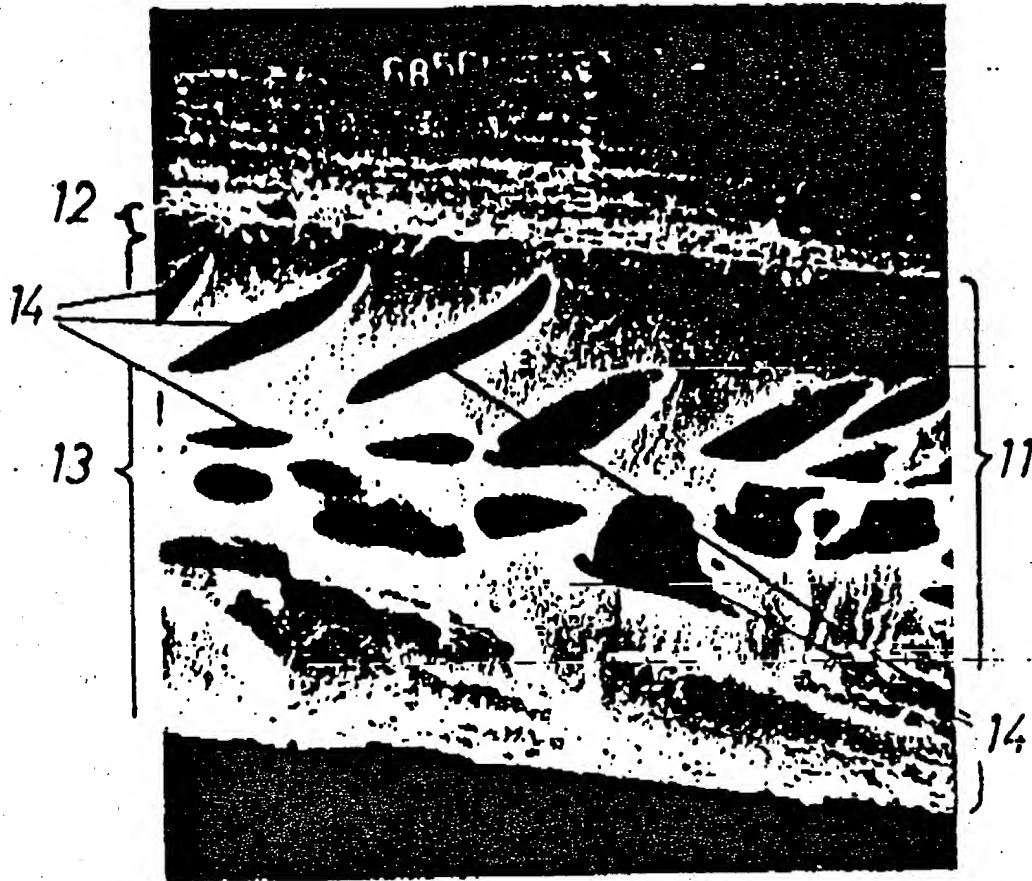


Fig.3

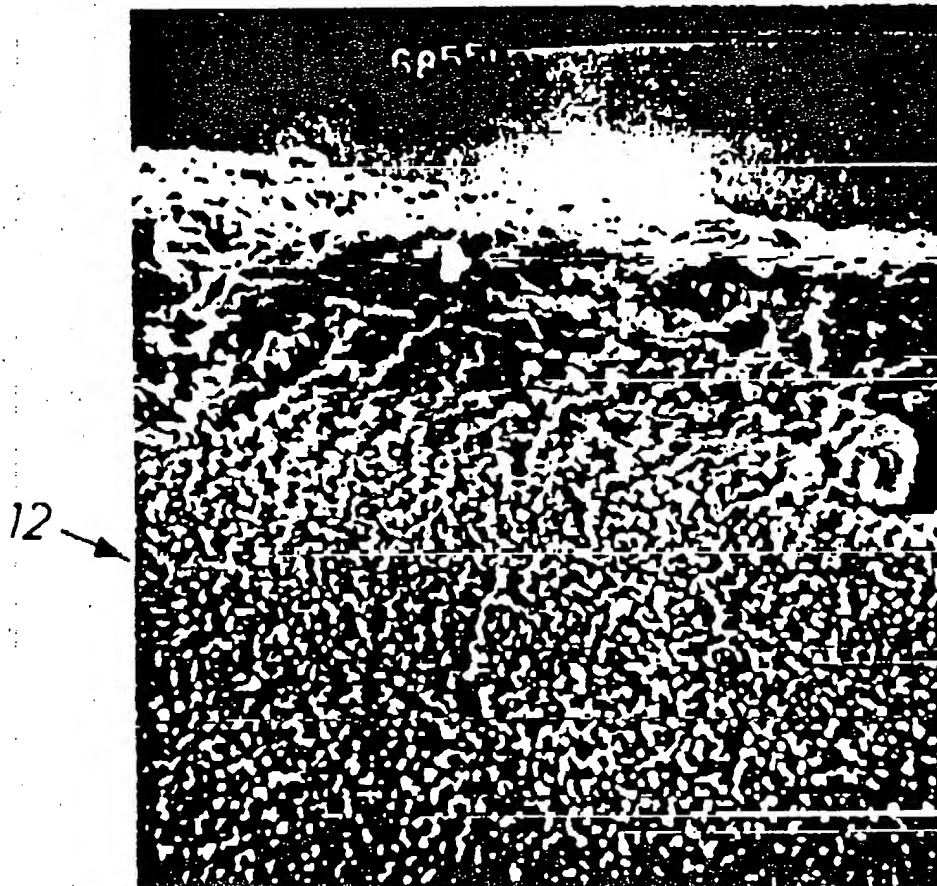


Fig.4

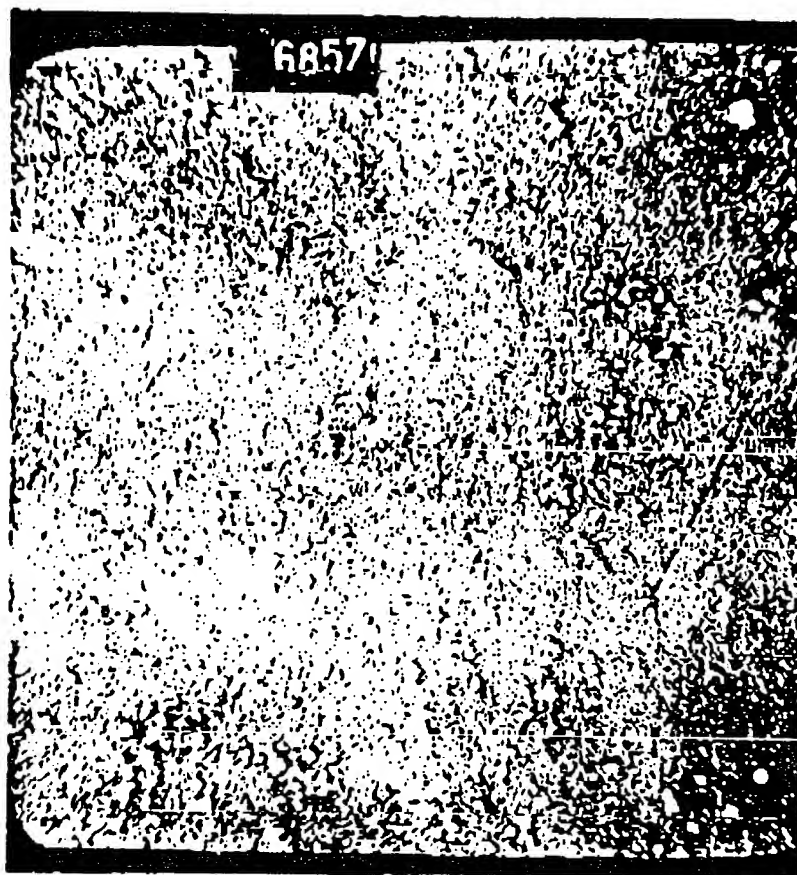


Fig.5



Fig. 6

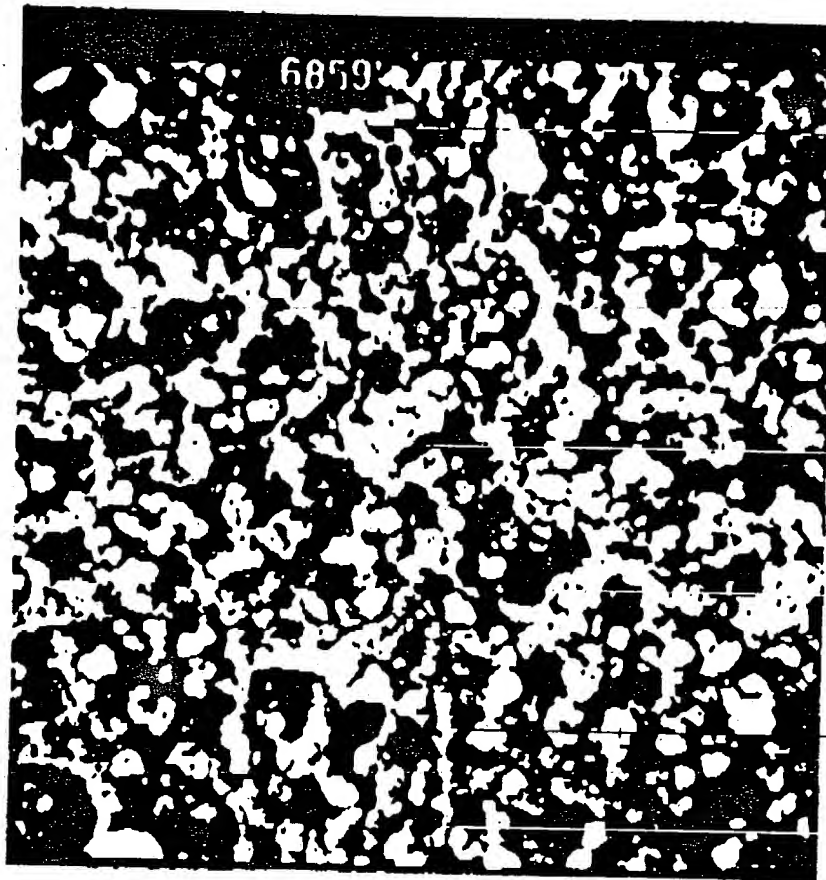
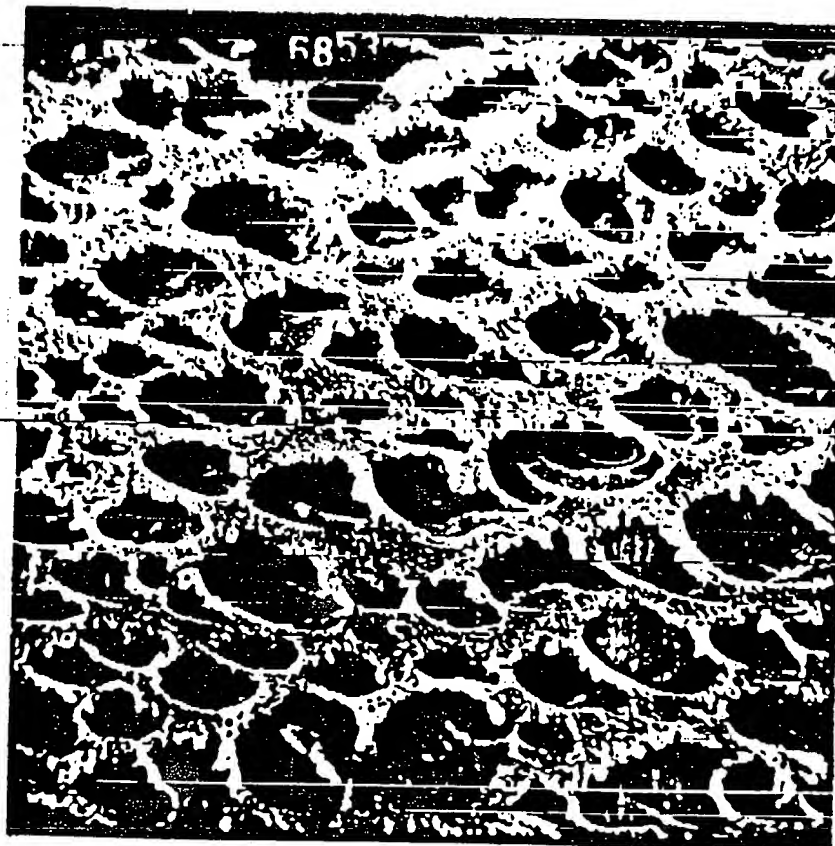


Fig. 7



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Fig. 8

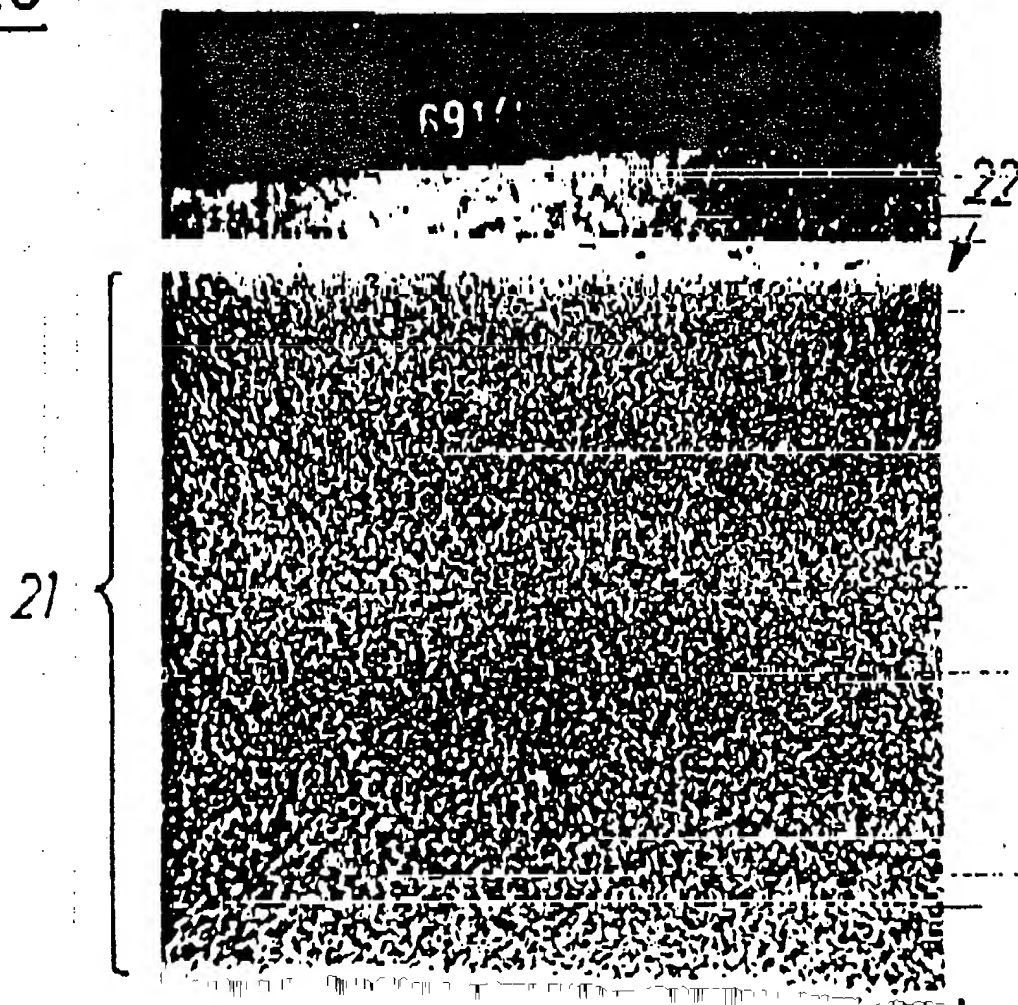


Fig.9

22 →

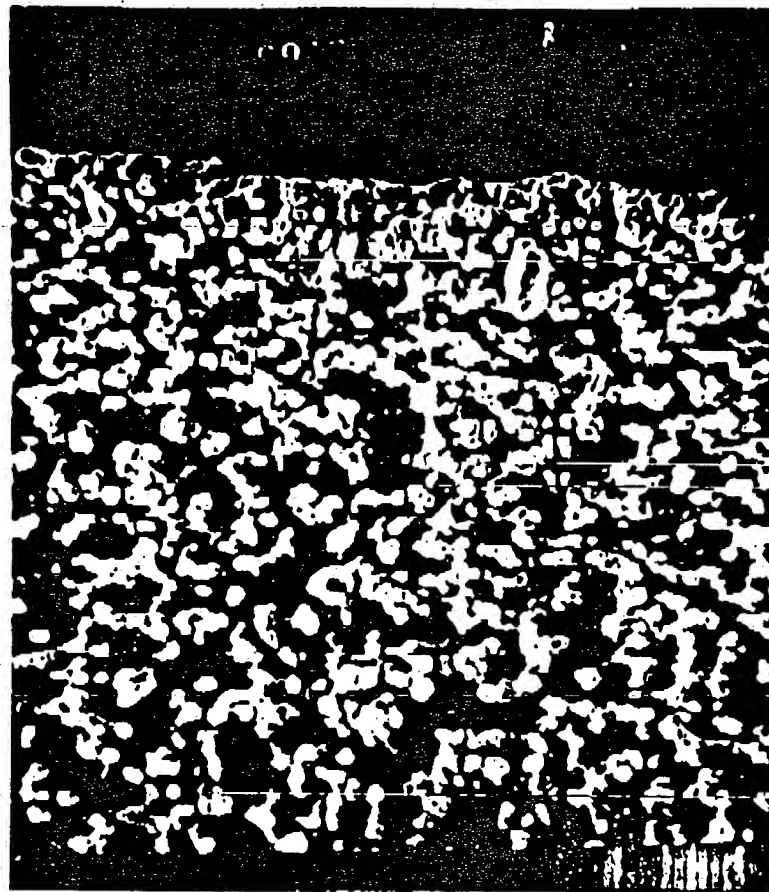


Fig.10

23 →



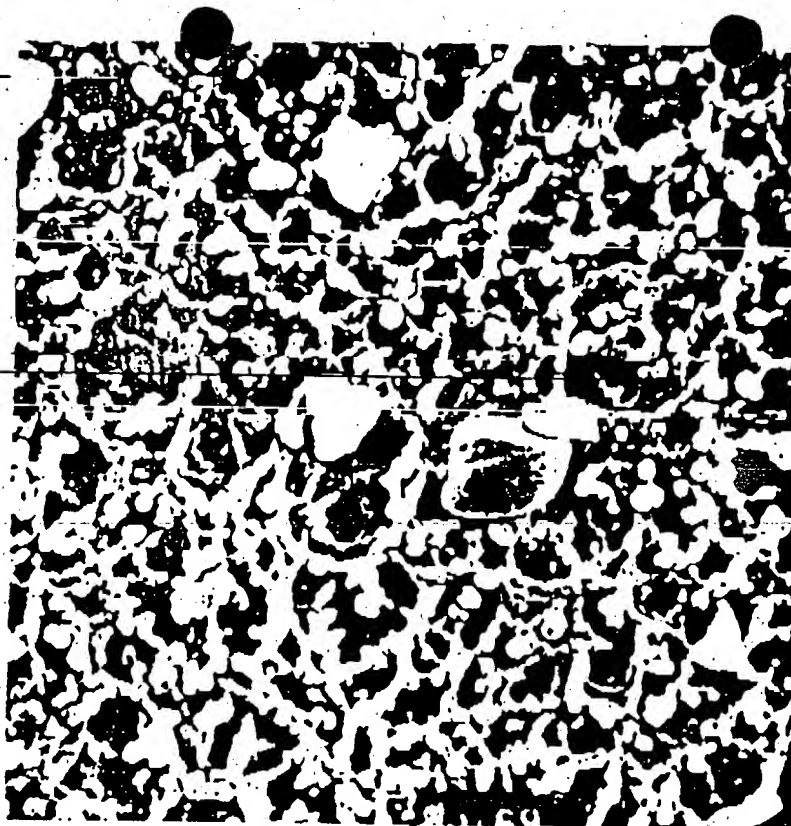


Fig.12

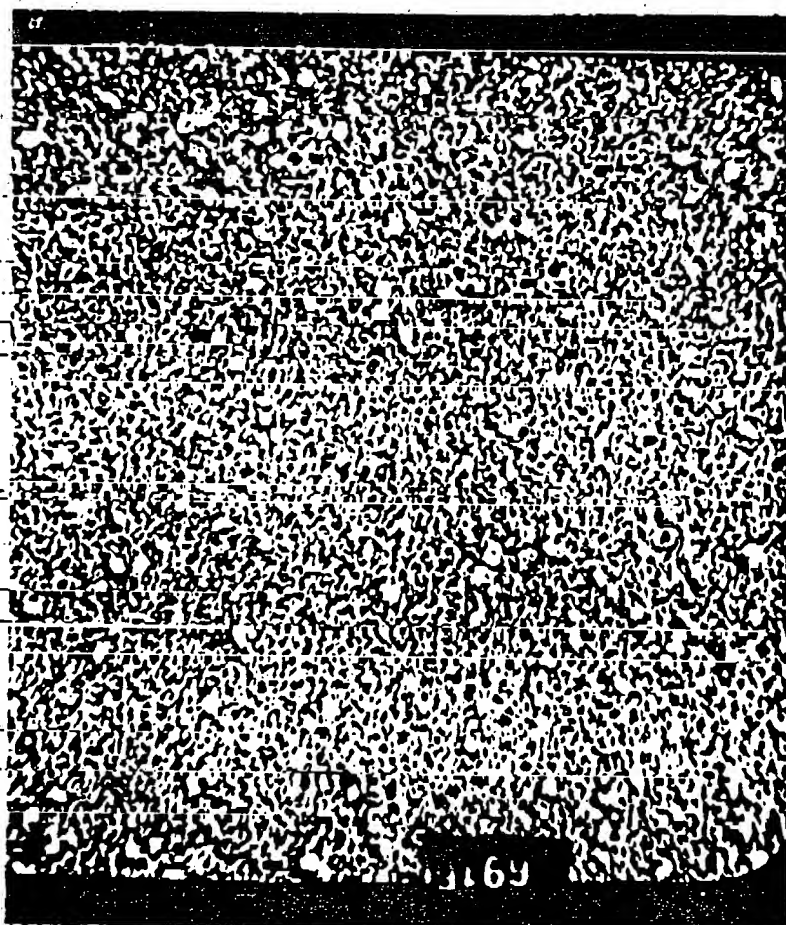


Fig.11

Fig.13

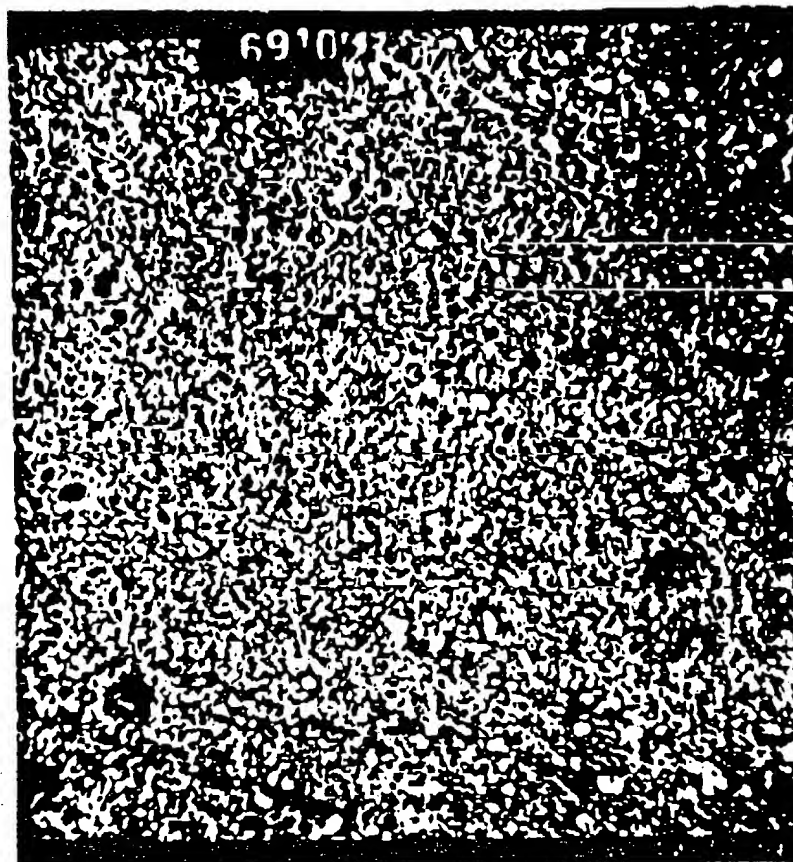
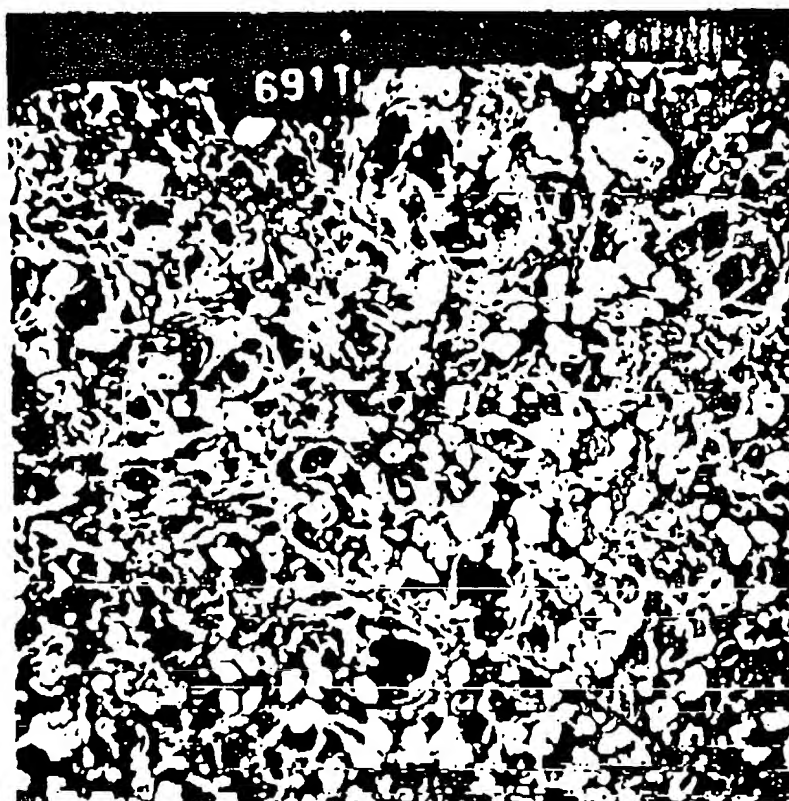


Fig.14



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SPECIFICATION

Process for the production of filter elements based on polysulphone

This invention relates to the production of filter elements based on polysulphone, in the form of filter membranes, membrane/deep filter combinations or filter bodies by a process in which a semi-finished filter element is formed from a solution of polysulphone containing a pore former and the polysulphone of this semi-finished product is coagulated by immersion in a liquid bath. —

Such a process for the production of anisotropic membranes is known from European Patent Application 1 301 074.1/0036315. This process is said to be suitable for the production of filter membranes, filter elements from polysulphone. For this purpose, a solution of polysulphone, molecular weight 3,500, in dimethyl formamide with the addition of isopropyl alcohol is shaped to form a membrane and immediately after it has been shaped or cast it is coagulated in water which is maintained at the surrounding temperature. This process, however, cannot be used for obtaining controlled and previously calculated or determined properties of the filter membrane as regards its porosity, pore size or cell structure. It is therefore proposed in European Patent Application 81 301 074.1/0036315 to obtain different properties in the filter membranes by producing the filter membranes from different resins or resin mixtures. In particular, the process disclosed in European Patent Application 81 301 074.1/0036315 can only be used for producing filter membranes with a highly anisotropic structure.

By contrast, it is an object of the present invention to provide a process for the production of polysulphone-based filter elements in which the nature of the cell structure and the porosity and pore size of the filter element can be predetermined by a simple and easily controlled modification of only a few process parameters independently of one another, and the nature of the cell structure can be controlled by different process parameters from those used for the porosity and pore size of the filter element.

To solve this problem in accordance with the invention, the proportions in which polysulphone, solvent and pore former are mixed in the polysulphone solution are determined according to the desired porosity and pore size of the filter element, and coagulation with stabilization of the filter element is carried out in the liquid bath over a period of about 30 seconds to 240 seconds.

at temperatures from below 0°C to about 15°C for forming filter elements with a pore size of from 0.1 nm to 1 nm in the active separating layer for the separation of macromolecules by ultrafiltration or

at temperatures of about 15°C to 45°C for forming filter elements with an asymmetric cell structure and a pore size in the active filter layer of from 0.05 µm to 10 µm for separating particles by microfiltration or

at temperatures from about 45°C to 80°C for forming filter elements with a symmetric cell structure and a pore size of from 0.05 µm to 10 µm for the separation of particles by microfiltration

and the filter element is then washed in at least one other liquid bath.

In the process according to the invention, therefore, the nature of the cell structure is determined mainly by the temperature maintained in the coagulation and stabilization bath but the choice of the particular temperature has virtually no influence on the porosity or pore size in the filter element. The process according to the invention is particularly distinguished by the fact it is highly reproducible.

The invention provides a clear separation between control of the cell structure and control of the porosity and pore size in the filter element. It has been found that the temperature control of the coagulation and stabilization bath, which influences the nature of the cell structure, has no significant influence on the porosity and pore size in the filter element. The latter features, which are important for the filter element, are mainly influenced by the composition of the polysulphone solution, in particular the proportions in which

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One possible method of producing similar filter elements in accordance with the invention consists, for example, of forming the semi-finished filter element by impregnating a woven or non-woven web with the polysulphone solution containing pore former.

The semi-finished filter element may also be formed by extruding the polysulphone solution containing pore former to produce a film in the form of a band or tube.

According to another example of producing the desired filter elements, a coarsely porous filter body which has been produced by sintering or some other means is steeped in or impregnated with the polysulphone solution containing pore former to form a semi-finished filter element, which is then transferred to the liquid bath for coagulation and stabilization of the polysulphone filling, optionally after pre-strengthening of its polysulphone filling in air.

According to the invention, the coagulation and stabilization bath may consist of water. Various additives may be introduced into the water of the coagulation and stabilization bath, either singly or in combination, e.g. solvents and/or pore formers and/or alcohol. Thus the same solvent as that used for the polysulphone solution may be added to the coagulation and stabilization bath in quantities of from 5 volumes % to 20 volumes %, preferably about 10 volumes %. Furthermore, for example, the same pore former as that used in the polysulphone solution may be added in quantities of about 1 volume % to 35 volumes %, preferably 10 volumes % to 20 volumes %.

Ethyl alcohol may also be added to the water of the coagulation and stabilization bath in quantities of about 5 volumes % to 20 volumes %, preferably about 10 volumes %. Instead of ethyl alcohol, comparable quantities of isopropyl alcohol may be added to the water of the coagulation and stabilization bath.

Examples of the invention are described in more detail below with reference to the drawings, in which

Figure 1 is a graphic representation of the rates of flow of water through the membranes produced according to the invention, measured per unit surface area, in dependence upon the temperature of the coagulation bath used in the formation of the membrane;

Figures 2 to 7 are electron microscopic photographs of a filter membrane produced by the process according to the invention at a coagulation bath temperature of 12°C, and...

Figures 8 to 14 are electron microscopic photographs of a filter membrane produced by the process according to the invention at a coagulation bath temperature of 50°C.

30 EXAMPLE 1

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A polysulphone solution having the following composition:

EXAMPLE 2:

A polysulphone solution having the following composition:

- 15.3% by weight polysulphone, molecular weight 1700,
- 24.4% by weight N-methyl pyrrolidone as solvent and
- 60.7% by weight polyethylene glycol, molecular weight 400, as pore-former

was cast on a smooth as in example 1 to form a layer having a thickness of about 200 μm to 500 μm (of wet film). After casting, the solution was kept in moist air (atmospheric humidity 50 to 80%) for about 30 seconds to 1 minute. The film obtained was then tested in a coagulation bath containing water in Example 1; the bath being adjusted to different temperatures in successive experiments as indicated below to produce membranes with different properties:

Experiment 2.1 bath temperature 15°C

Experiment 2.2 bath temperature 20°C

Experiment 2.3 bath temperature 30°C

Experiment 2.4 bath temperature 40°C

Experiment 2.5 bath temperature 50°C

Experiment 2.6 bath temperature 70°C

Stable filter membranes were obtained in all the experiments after washing as in Example 1, and these membranes were then investigated for their characteristic properties.

Permeability of the filter membranes to water: The water permeability of the membranes was determined as a major indication of the cell structure, porosity and pore size. This was done by measuring the rate of flow of water through each membrane per unit surface area and unit time. Previously filtered, distilled water was used as test medium and the pressure drop across the membrane was adjusted to 0.9 bar.

In the graph of Figure 1, the rate of through-flow of water is given in

$$\frac{\text{ml}}{\text{cm}^2} \times \text{min} \times 10^{-3}$$

in dependence upon the temperature of the coagulation bath.

Figure 1 contains two graphs. The graph labelled "mixture 1" relates to filter membranes produced according to Example 1 while the graph labelled "mixture 2" relates to filter membranes produced according to Example 2.

Both graphs show that the relationship between the rate of through-flow of water and the temperature of the coagulation bath is virtually linear at temperatures from 10°C to about 40°C. The higher the temperature of the coagulation bath, the greater is the rate of flow of water through the membranes of both groups. At coagulation bath temperatures above 40°C, the rate of through-flow of water continues to increase with increasing temperature of the coagulation and stabilization bath but the rate of increase is less rapid than at temperatures up to 40°C of the coagulation and stabilization bath.

Electron microscopic photograph of the structure: Figures 2 to 14 are electron microscopic photographs of membranes produced from polysulphone solution according to Example 1. Figures 2 to 7 are electron microscopic photographs of a polysulphone filter membrane produced with the coagulation bath maintained at 12°C. Figure 2 shows a cross section through the edge of such a membrane in 180 times enlargement (479.6 times). As may be seen from Figure 2, the membrane 11 has a closed skin 12 on its upper side and underneath this a substructure 13 with finger shaped holes 14. Figure 3 shows a section of the skin 12 on the surface of the membrane 11 in 7500 times enlargement (7506 times). The structure of this surface skin is so dense that the membrane has all the properties of an ultra filtration membrane. The almost completely closed structure of the surface skin may be seen from Figures 4 to 6 which are electron microscopic photographs of the closed upper side of the filter membrane 11, Figure 4 being a 750 times enlargement (748 times), Figure 5 a 7500 times enlargement (7506 times) and Figure 6 a 15,000 times enlargement (15,012 times). These electron microscopic photographs on different scales show, in conjunction with Figures 2 and 3, that a virtually pore-free surface layer is formed, which is impermeable to water used as test medium. As may be seen from Figure 1, virtually complete imperviousness of the surface

Figures 8 to 14, by contrast, show a filter membrane with an almost symmetrical porous structure produced according to experiment 1.4 of Example 1, namely with the coagulation and stabilisation bath maintained at a temperature of 50°C. Filter membrane 21 obtained in this manner is a typical micro filtration membrane, i.e. a membrane which has an almost symmetrical porous structure throughout its thickness

between the two surfaces 22 and 23.

Figure 8 is an electron microscopic photograph showing this microfiltration membrane 21 in cross section through an edge enlarged 740 times (740 times). It may be seen from Figure 8 that the pores are possibly slightly smaller in the region of the upper surface 22 than in the region of the lower surface 23 but it is clear that the pore structure is substantially symmetrical throughout. The fact that the differences in pore size between the region of the upper surface 22 and the region of the lower surface 23 are only slight is evident from a comparison of Figures 9 and 10 which are electron microscopic photographs of edge cross sections through the microfiltration membrane 21, Figure 9 being taken in the region of the upper surface 22 and Figure 10 in the region of the lower surface 23.

Figure 11 is an electron microscopic photograph of the microfiltration membrane 21 of Figure 8 taken from the upper surface, i.e. showing the upper surface 22 in 1100 times enlargement (1100 times). It may be seen from Figure 11 that the pores of the microfiltration membrane 21 open on to the upper surface of the membrane. A comparison with Figure 13 shows that exactly the same conditions also prevail on the lower surface of the microfiltration membrane 21. If one takes into account that Figure 13 is an electron microscopic photograph of the underside of the membrane enlarged 750 times (750.75 times), the comparison between Figures 11 and 13 reveals that the openings of the pores on the underside of the microfiltration membrane 21 are not significantly larger than on the upper side. Figure 12 is an electron microscopic photograph of the upper side of the microfiltration membrane 21 of Figure 8 enlarged 7500 times (7480 times) and shows a more or less regular framework structure of the membrane matrix. The structure of the matrix on the underside of the membrane 21, on the other hand, is slightly less regular, as may be seen from Figure 14 (electron microscopic photograph in 3000 times enlargement (2945.8 times)). However, no significant difference in porosity and pore size can be detected between Figures 12 and 14.

The film thicknesses given in connection with the exemplary embodiments described above and the casting speeds of from 0.5 m to 1.0 m per minute provided in these examples depend to a certain extent on the construction and dimensions of the laboratory installations used for carrying out the experiments. Whereas a final membrane thickness of about 70 µm, which is the value which can be achieved in such installations, is sufficient for ultra-filtration membranes, the possibility of also obtaining greater thicknesses would be desirable for symmetric membranes, and this may be achieved by suitable design of the production plant.

35. CLAIMS

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1. Process for the production of filter elements based on polysulphone, in the form of filter means selected from filter membranes, membranes deep filter combinations or filter modules, in which process a semi-finished filter element is formed from a solution of polysulphone containing a pore former and the polysulphone of this semi-finished product is coagulated by immersion in a liquid bath, wherein the proportions in which polysulphone, solvent and pore former are mixed in the polysulphone solution are adjusted according to the desired porosity and pore size of the filter element, and wherein coagulation with stabilisation of the filter element is carried out in the liquid bath for a period of about 30 seconds to about 240 seconds and
 - a) at a temperature from below 0°C to about 15°C for forming filter elements having a pore size of from 0.1 nm to 1 nm in the active separating layer for separating macromolecules by ultra filtration or
 - b) at temperatures from about 15°C to about 45°C for forming filter elements with an asymmetric cell structure and a pore size of the active separating layer from 0.05 µm to 10 µm for separating particles by microfiltration or
 - c) at temperatures in the range from about 45°C to 80°C for forming filter elements with a symmetric cell structure and pore size of from 0.05 µm to 10 µm for separating particles by microfiltration

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6. Process according to any one of the claims 1 to 3, wherein the semi-finished filter element is formed by impregnating a woven or non-woven web with the polysulphone solution containing pore former.

7. Process according to any one of the claims 1 to 3, wherein the semi-finished filter element is formed by extruding the polysulphone solution containing pore former to form a band or tube of film.

8. Process according to any one of the claims 1 to 3, wherein the semi-finished filter element is formed by soaking or impregnating a coarse porous filter body produced by sintering or some other means with the polysulphone solution containing pore former and wherein this semi-finished filter element is transferred to a liquid bath for coagulation and stabilization of the polysulphone filling, optionally after prestrengthening of its polysulphone filling in air.

9. Process according to any one of claims 1 to 8, wherein the coagulation and stabilization bath contains water with the addition of solvents and/or pore formers and/or alcohol. 10

10. Process according to claim 9, wherein the coagulation and stabilization bath contains an addition of the same solvent as that used for the polysulphone solution, in quantities of from 5 volumes % to 20 volumes %, preferably about 10 volumes %.

11. Process according to claim 9 wherein the coagulation and stabilization bath contains an addition of the same pore former as the polysulphone solution in quantities from about 1 volume % to 35 volumes %, preferably from 10 volumes % to 20 volumes %. 15

12. Process according to one of the claims 9 wherein the coagulation and stabilization bath contains an addition of ethyl alcohol in quantities of from 5 volumes % to 20 volumes %, preferably about 10 volumes %.

13. Process according to one of the claims 9 wherein the coagulation and stabilization bath contains an addition of isopropyl alcohol in quantities from about 5 volumes % to 20 volumes %, preferably about 10 volumes %. 20

14. Process according to claim 1 wherein washing with water is carried out in one or more baths at temperatures from 20°C to 40°C over a period of from 30 minutes to several hours.

15. Process according to claim 1 wherein a mixture is prepared from 10 to 18% by weight of polysulphone, having a molecular weight of 1700 to 28% by weight of N-methylpyrrolidone as solvent, the remainder being polyethylene glycol having a molecular weight of 400, as pore former, a semi-finished product having the form of the desired filter element is produced from this polysulphone solution, this semi-finished product is prestrengthened in moist air for a period of from 30 to 60 seconds, the semi-finished product is then coagulated and stabilized in a liquid bath which is maintained at a temperature selected according to the desired structure of the filter element to be produced, and the filter element is then washed in water. 25 30

16. Process according to claim 15, wherein the polysulphone solution is poured out to form a layer having a thickness of 200 µm or more (thickness of the wet layer) to produce filter membranes.